

# Using Soil Phosphorus Profile Data to Assess Phosphorus Leaching Potential in Manured Soils

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## ABSTRACT

Transport of P by subsurface flow pathways can be an important mechanism of P transfer from land to water, particularly in manured soils that are artificially drained. This study was conducted to determine whether detailed description and interpretation of soil P profile data provide adequate insight into P leaching potential. Evidence of P translocation within soil profiles of a tile-drained Buchanan (fine-loamy, mixed, semiactive, mesic Aquic Fragiudult)-Hartleton (loamy-skeletal, mixed, active, mesic Typic Hapludults) catena was assessed by measuring oxalate-extractable P, P sorption saturation, Mehlich-3 P, water-extractable P in bulk and clay film samples obtained from individual horizons. Tile-drain monitoring and column leaching experiments were conducted to evaluate interpretations derived from soil P profile data. Soil P fractions were not correlated with P losses in lysimeter studies, indicating the limited potential of using soil profile P data for quantitative prediction of leaching losses. Application of manure to the soil surface resulted in significant increases in leachate P concentrations from the lysimeters. Soil profile P data did, however, provide some evidence of long-term P leaching. While bulk horizon samples did not indicate significant long-term P translocation to soil depths corresponding with artificial drainage, some clay film samples had significantly elevated oxalate P, P sorption saturation and Mehlich-3 P at lower depths. Elevated P concentrations in clay films may be associated with preferential transport of P along soil macropores, although, not all clay films sampled in this study were necessarily associated with active macropores. Thus, soil P profile data appear to provide limited insight into P leaching potential.

PHOSPHORUS, AN ESSENTIAL nutrient for crop and animal production, can accelerate freshwater eutrophication (Carpenter et al., 1998). The USEPA (1996) identified eutrophication as the most ubiquitous water quality impairment in the USA, with agriculture a major contributor of P (U.S. Geological Survey, 1999). Current efforts to reduce P losses from agricultural lands target critical source areas of P transport, where high concentrations of P are found in soils prone to surface runoff (Sharpley et al., 1994) or subsurface macropore flow (Sims et al., 1998). Identifying soils where P leaching can contribute to surface water P loading remains an important scientific need given the general paucity of data connecting specific soils with subsurface P transport.

Direct observation of P leaching can be difficult, since leaching losses often occur in discrete events, or pulses, that can be easily missed; continuous flow-monitoring equipment is expensive. Traditional measures of leaching potential used for N, such as saturated hydraulic conductivity, may not be applicable to P leaching poten-

tial, as they emphasize matrix rather than macropore flow. For instance, preferential flow through macropores may be aggravated by low saturated hydraulic conductivity, as water is locally forced through macropores (Chardon and van Faassen, 1999).

While surface runoff has long been seen as the dominant pathway by which P is transported from land to water, subsurface flow pathways can be important to P transport in certain landscapes (Sharpley and Halvorson, 1994). For instance, subsurface P transport has been well documented through sandy soils (Sims et al., 1998), well-structured, fine-textured soils with tortuous macropores (Chardon and van Faassen, 1999; Djodjic et al., 1999) and porous organic soils with low P sorption capacities (Miller, 1979; Cogger and Duxbury, 1984). Subsurface transport is undoubtedly dominated by preferential flow through soil macropores (Simard et al., 2000), and environmentally important losses to surface waters are facilitated by the introduction of artificial drainage, which provides lateral connectivity between subsurface macropores and surface water (Dils and Heathwaite, 1999). In addition, factors such as soil P sorption saturation ( $P_{\text{sat}}$ ) and oxidation-reduction cycles can greatly increase P mobility through soils (Behrendt and Boekhold, 1993; Heckrath et al., 1995).

Where no direct P leaching data exist, investigators have turned to evidence of long-term P translocation within soil profiles as an indicator of P leaching potential (Kuo and Baker, 1982; Mozaffari and Sims, 1994; Eghball et al., 1996). Often, P profile data from reference soils with little to no history of P additions are compared with P profile data from similar soils with histories of P amendment. For instance, Eghball et al. (1996) concluded that significant leaching of P had occurred in a sandy loam soil (a Typic Haplustoll) because of elevated P concentrations in the subsoil horizons of soils receiving manure and mineral P applications. Elsewhere, Mozaffari and Sims (1994) and Kuo and Baker (1982) derived similar conclusions after comparing P profile data from unmanured and manured members of various mineral and organic soils (Aquic Hapludults, Typic Umbraqualls, Typic Fluvaquents, Terric Medisaprists).

In contrast to those inferential studies reporting accumulations of subsurface P because of leaching, Thomas et al. (1997) observed significant leaching of P through a silty clay loam soil but little accumulation of P with depth. Similarly, Haygarth et al. (1998) observed total P (TP) concentrations in leachate of up to  $0.89 \text{ mg L}^{-1}$  from a heavily manured Typic Haplaquept with little evidence of P translocation below the Ap horizon. One

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**Abbreviations:**  $\text{Al}_{\text{ox}}$ , oxalate-extractable Al; DRP, dissolved reactive P;  $\text{Fe}_{\text{ox}}$ , oxalate-extractable Fe;  $\text{P}_{\text{ox}}$ , oxalate-extractable P;  $\text{P}_{\text{sat}}$ , P sorption saturation; PVC, polyvinyl Cl; TP, total P.

reason that P profile data may not reveal evidence of P translocation, and therefore may provide an incomplete picture of P leaching potential, is that translocated P may be concentrated along preferential flow pathways (e.g., Hansen et al., 1998).

Data obtained from bulk soil samples favor detection of P translocated under matrix flow. As bulk sampling of soils homogenizes ped interiors with the walls of macropores, P sorbed to macropore walls may be sufficiently diluted by mixing that it is not detected. Sharpley et al. (1993), for instance, found little evidence of subsurface P accumulation in any of twelve heavily fertilized Oklahoma soils with 12 to 35 yr of poultry litter application. Possibly, bulk soil sampling diluted areas of P concentration thereby masking differences between manured and unmanured sites.

The objective of this study was to determine whether soil P profile data could be reliably used to assess P leaching potential in heavily manured soils. Bulk and clay film samples collected from soil horizons were analyzed for evidence of P translocation. To validate conclusions drawn from P profile data, tile-drain monitoring data and column leaching experiments were assessed.

## MATERIALS AND METHODS

### The Study Area and Sampling Protocol

The study area falls within the Susquehanna River Basin, part of the Appalachian Valley and Ridge Physiographic Province of the northeastern USA (Fig. 1). A hillslope of Buchanan and Hartleton soils within FD-36, an intensively monitored watershed within the Susquehanna River Basin, was selected for study (Fig. 2). The hillslope is located within a conventionally tilled field under corn (*Zea mays* L.)-soybean (*Glycine max* Merr.)-wheat (*Triticum aestivum* L.) rotational cropping. Approximately  $5 \text{ Mg ha}^{-1} \text{ yr}^{-1}$  poultry (*Gallus gallus domesticus* L.) manure, corresponding to  $85 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ , is applied annually to soils in the area prior to cultivation (Gburek et al., 2000). A 15-cm ceramic tile line, established approximately 35 yr ago at a depth of 50 to 60 cm, drains lower positions on the hillslope.

Three 2-m deep pits were excavated along the hillslope with slope gradients ranging from 4 to 18% (Fig. 2). Profile morphology was described (Table 1) following standard U.S. Natural Resource Conservation Service protocol (Soil Survey Staff, 1993), and intact

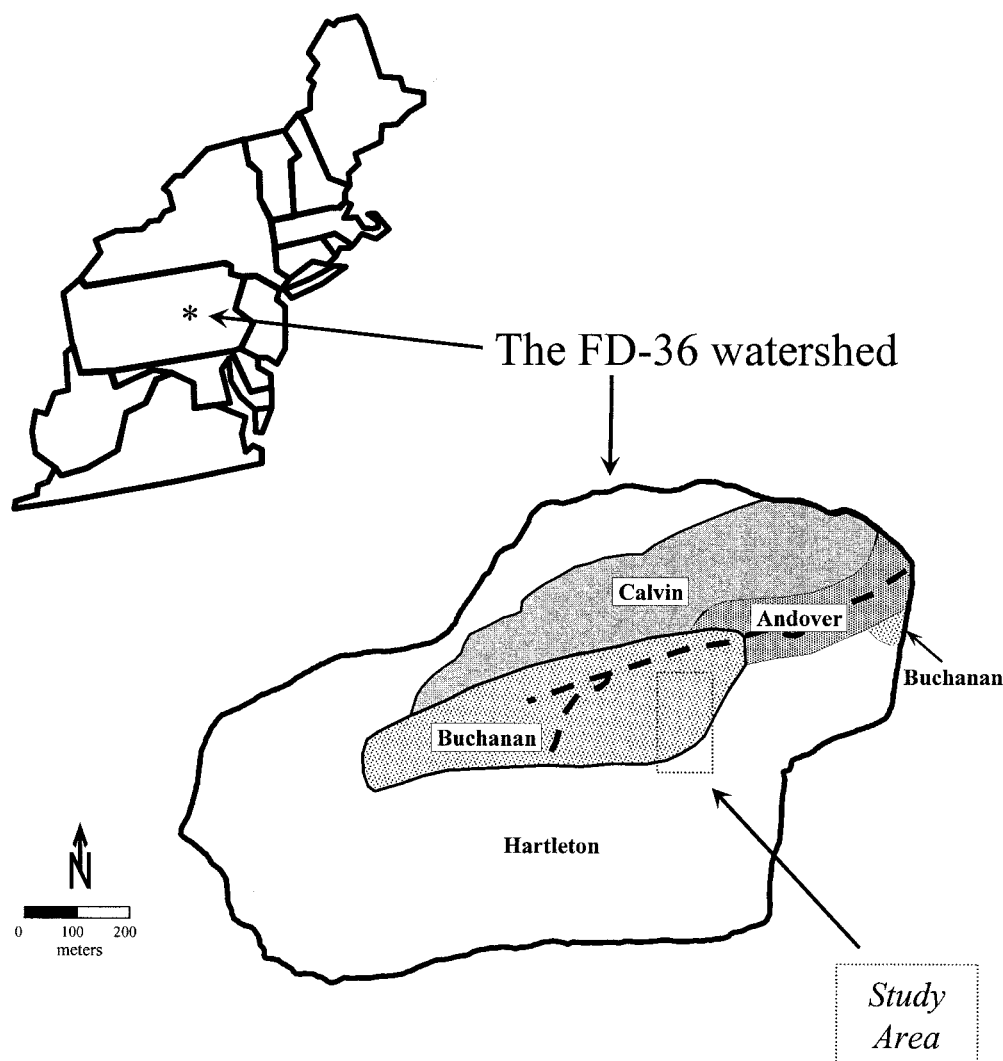


Fig. 1. Location of study area and distribution of soils within the FD-36 watershed, central Pennsylvania.

samples were collected from each horizon for laboratory analysis. Soil samples were stored at 4°C prior to analysis.

The two soils found lower in the hillslope were formed in interstratified sandstone and shale colluvium. Colluviation likely occurred under periglacial climatic conditions during the Wisconsin glacialiation. These soils, labeled Lower Buchanan and Upper Buchanan, are taxadjuncts (Soil Survey Staff, 1999); they fit all criteria of the Buchanan series except drainage. They are somewhat poorly drained while the Buchanan series is moderately well drained (there is no somewhat poorly drained series in this catenary sequence). Also, the Lower Buchanan has a loamy-skeletal family particle-size class. The third soil was formed in residuum, at the outer edge of a transition zone between colluvium and residuum. This soil is assigned to the Hartleton series. No water-table data were available to determine if this soil should be designated as Oxyaquic.

To assess subsurface losses from the hillslope, the tile-drain outlet was equipped with an automatic sampler in May 2000 (Sigma 900 Max Portable Sampler, HACH/American Sigma Company, Loveland, CO<sup>1</sup>) and programmed to collect flow-weighted composite samples of tile drainage. In addition, in December 2000, intact soil columns were collected adjacent to each of the profile description pits following the method of McDowell and Sharpley (2001a). A 30-cm diameter polyvinyl Cl (PVC) cylinder was pushed into the soil by constant pressure from a 2-Mg drop weight. To prevent surface compaction, the drop weight was not allowed to contact the soil surface and no visual evidence of compaction was observed following cylinder insertion into the soil. Columns were removed by excavating the soil adjacent to the submerged cylinder and then tilting the cylinder to cleanly break contact between the soil column and the underlying subsoil. Two 30-cm deep columns and two 50-cm deep columns were collected from each of the three locations.

### Ped Dissection

Intact peds from each horizon were dissected with stainless steel scalpels to physically separate compo-

nents (Buol and Hole, 1959). Subsoil horizons were carefully dissected, or scraped, to separate clay films, from the intact peds. Following dissection, samples were air dried prior to laboratory analysis. In all horizons, except for the Hartleton 2Bt4 horizon, which could not be sampled, the clay films of the argillic horizons are thick and distinctly colored. We do recognize that there was some contamination of soil components during the scraping process. However, because of the distinct morphological features, we believe that these soils lend themselves to effective ped dissection.

### Leaching Experiments

Preparation of the columns for leaching experiments followed the method of McDowell and Sharpley (2001b). Figure 3 illustrates the design of the intact cores. To prevent by-pass flow between the soil and the PVC cylinder, soils were allowed to dry for several weeks to induce shrinkage. Once dry (at approximately the permanent wilting point), a void of approximately 0.5-cm width appeared between the soil and the cylinder. The lower end of the void was sealed with nonreactive silicone. Paraffin wax was then poured into the void, effectively sealing the interface between soil and cylinder (Fig. 3). Following this procedure, the bottom of the column was supported by a layer of cheese cloth and a 30-cm diam. PVC disk, perforated with roughly 60, 0.2-cm perforations. The disk, in turn, was held in place by a PVC cap sealed to the cylinder with silicone. To allow drainage, a hole was drilled into the cap and fitted with a 1-cm PVC nipple that could be inserted into a plastic collection container (Fig. 3). This design ensured that drainage did not become reductive during the leaching experiments.

Two experiments were conducted on the soil columns to directly assess P leaching potential. In the first experiment, soils were leached prior to manure addition. The last field application of manure to these soils was 9 mo before the leaching experiment. In the second experiment, poultry manure was applied to the soil surface at a TP application rate of 85 kg ha<sup>-1</sup>, representing a typical P application for the site. Leaching experiments were conducted 1 d after manure application. Properties of the poultry manure are given in Table 2.

To control antecedent moisture between soil columns as well as between the two experiments, soil columns were wet to surface saturation (approximately one pore volume) and then allowed to drain for 48 h (field capacity) before the leaching experiments were initiated. Poultry manure was applied to soil at field capacity. Soil columns were irrigated with a Raindrip R580 Drip Watering Soaker system (Raindrip Inc., Chatsworth, CA) delivering water at 0.6 cm h<sup>-1</sup>. As estimated infiltration capacities of Hartleton and Buchanan soils range from 1.2 to 15 cm h<sup>-1</sup> (Eckenrode, 1985), no ponding occurred during the leaching experiments. Soils were drip irrigated every 6 h (2.4 cm d<sup>-1</sup>) for 72 h, resulting in a total application of 7.5 cm (5.3 L) over the study period. This wetting regime corresponds with a precipi-

<sup>1</sup> Mention of trade names does not imply endorsement by the USDA.

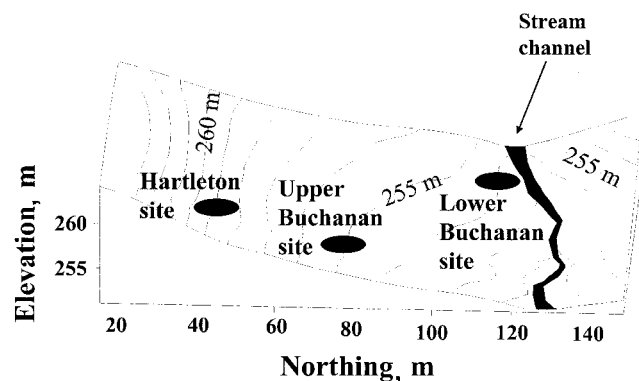


Fig. 2. Map of study area showing 1-m contours and location of sampling sites.

**Table 1. Morphological descriptions of soils included in the study.**

Lower Buchanan	Upper Buchanan
<p><b>Ap1</b>—0 to 12 cm; brown (10YR 5/3; 10YR 6/2 dry) very channery silt loam; weak fine and medium granular structure; slightly sticky, slightly plastic; few, medium roots throughout horizon; many tubular discontinuous fine and medium and few very coarse tubular pores; 25% subangular blocky mixed shale and sandstone channers and 20% subrounded mixed shale and sandstone gravels; slightly acid (pH 6.5); abrupt smooth boundary.</p> <p><b>Ap2</b>—12 to 25 cm; brown (10 YR 5/3) very channery silt loam; weak fine and medium subangular blocky structure; slightly sticky, slightly plastic; very few, very fine roots throughout horizon; many tubular discontinuous fine and medium and few very coarse tubular pores; 25% subangular blocky mixed shale and sandstone channers and 20% subrounded mixed shale and sandstone gravels; neutral (pH 7.0); abrupt smooth boundary.</p> <p><b>Bt1</b>—25 to 45 cm; brown (7.5 YR 5/4) very channery silty clay loam; weak medium and coarse subangular blocky structure; sticky, plastic; many medium and coarse prominent pale brown (10YR 6/3) Fe depletions and many medium and coarse prominent strong brown (7.5 YR 5/6) masses of Fe accumulation in the matrix; few fine spherical Fe nodules; common distinct brown (10 YR 5/3) clay films on faces of peds; common medium and coarse irregular pores; 25% subangular blocky mixed shale and sandstone channers and 20% subrounded mixed shale and sandstone gravels; slightly acid (pH 6.5); clear wavy boundary.</p> <p><b>Bt2</b>—45 to 62 cm; brown and light brown (7.5 YR 5/4 65%; 7.5 YR 6/3 35%) very channery silty clay loam; moderate medium and coarse subangular blocky structure; very sticky, very plastic; many extremely coarse prominent pinkish grey (7.5 YR 6/2) Fe depletions and many extremely coarse prominent strong brown (7.5 YR 5/6) masses of Fe accumulation in the matrix; common distinct brown (7.5 YR 5/4) clay films on faces of peds; common medium and coarse irregular pores; 25% subangular blocky mixed shale and sandstone channers and 20% subrounded mixed shale and sandstone gravels; strongly acid (pH 5.5); abrupt wavy boundary.</p> <p><b>2Btx1</b>—62 to 105 cm; reddish brown and brown (5 YR 4/4 60%; 7.5 YR 5/4 40%) extremely gravelly loam; weak extremely coarse prismatic structure parting to moderate medium and coarse subangular blocky structure; slightly sticky, slightly plastic; many coarse prominent pinkish gray (5 YR 6/2) Fe depletions and many medium and coarse prominent strong brown (7.5 YR 5/8) masses of Fe accumulation in the matrix; common distinct brown (7.5 YR 5/4) clay films on faces of peds; common coarse and very coarse irregular pores; 30% subangular blocky mixed shale and sandstone channers and 35% subrounded mixed shale and sandstone gravels; very strongly acid (pH 5.0); clear wavy boundary.</p> <p><b>2Btx2</b>—105 to 130 cm; reddish brown (5YR 4/4) extremely channery loam; weak extremely coarse prismatic structure parting to moderate medium and coarse subangular blocky structure; slightly sticky, slightly plastic; many coarse prominent pinkish gray (5 YR 6/2) Fe depletions and common medium and coarse prominent strong brown (7.5 YR 5/8) masses of Fe accumulation in the matrix; common distinct reddish brown (5 YR 4/4) clay films on faces of peds; common very coarse irregular pores; 35% subangular blocky mixed shale and sandstone channers and 30% subrounded mixed shale and sandstone gravels; strongly acid (pH 5.5).</p>	<p><b>Ap1</b>—0 to 15 cm; brown (10YR 5/3; 10YR 6/2 dry) silty clay loam; moderate fine and medium subangular blocky structure; slightly sticky, slightly plastic; few faint brown (10 YR 5/3) clay films on vertical ped faces; few fine and medium roots throughout horizon; many tubular discontinuous fine and few very coarse tubular pores; 2% subangular blocky mixed shale and sandstone channers; slightly acid (pH 6.5); abrupt smooth boundary.</p> <p><b>Ap2</b>—15 to 27 cm; brown (10 YR 5/3) silty clay loam; weak fine and medium subangular blocky structure; slightly sticky, slightly plastic; few faint brown (10 YR 5/3) clay films on vertical ped faces; few fine roots throughout horizon; many tubular discontinuous fine and few very coarse tubular pores; 2% subangular blocky mixed shale and sandstone channers; slightly acid (pH 6.5); abrupt smooth boundary.</p> <p><b>Bt1</b>—27 to 55 cm; strong brown and pinkish gray (7.5 YR 5/6 60%; 7.5 YR 6/2 40%) clay; moderate coarse angular blocky structure; sticky, plastic; many coarse prominent light brown gray (10YR 6/2) Fe depletions and many coarse prominent strong brown (7.5 YR 5/6) masses of Fe accumulation in the matrix; common discontinuous distinct dark yellow brown (10 YR 3/4) clay films on surfaces along pores and common discontinuous faint strong brown (7.5 YR 5/6) clay films on ped faces; few fine roots throughout horizon; tubular discontinuous fine pores; 5% subangular blocky mixed shale and sandstone channers; slightly acid (pH 6.5); clear wavy boundary.</p> <p><b>Bt2</b>—55 to 95 cm; pinkish gray and strong brown (7.5 YR 7/2 65%; 7.5 YR 5/6 35%) silty clay loam; moderate coarse angular blocky parting to massive structure; sticky, plastic; many very coarse faint pinkish grey (7.5 YR 7/2) Fe depletions and common coarse prominent strong brown (7.5 YR 5/6) masses of Fe accumulation in the matrix; many continuous prominent pinkish gray (7.5 YR 6/2) clay films on ped faces and common discontinuous prominent strong brown (10 R 7/4) clay films on vertical ped faces; common fine irregular pores; 1% subangular blocky mixed shale and sandstone channers; moderately acid (pH 6.0); abrupt wavy boundary.</p> <p><b>2Btx1</b>—95 to 120 cm; brown and reddish brown (7.5 YR 5/4 80%; 5 YR 4/4 20%) very gravelly silty clay loam; weak extremely coarse prismatic structure parting to subangular blocky structure; very sticky, very plastic; common coarse prominent pinkish gray (7.5 YR 6/2) Fe depletions and many coarse distinct strong brown (7.5 YR 5/6) masses of Fe accumulation in the matrix; common distinct discontinuous light brown (7.5 YR 6/4) clay films on surfaces along pores; common medium irregular pores; 10% subangular blocky mixed shale and sandstone channers and 35% subangular mixed shale and sandstone gravels; slightly acid (pH 6.5); clear wavy boundary.</p> <p><b>2Btx2</b>—120 to 160+ cm; brown (7.5YR 5/4) very gravelly clay loam; weak extremely coarse prismatic structure parting to weak coarse platy and moderate medium subangular blocky structure; slightly sticky, slightly plastic; common coarse prominent light brown (7.5 YR 6/3) iron depletions and few coarse distinct strong brown (7.5 YR 5/6) masses of Fe accumulation in the matrix; common distinct discontinuous light brown (7.5 YR 6/4) clay films on surfaces along pores; common medium irregular pores; 10% subangular blocky mixed shale and sandstone channers and 35% subangular mixed shale and sandstone gravels; moderately acid (pH 6.0).</p>
<p><b>Hartleton</b></p> <p><b>Ap1</b>—0 to 20 cm; brown (10YR 4/3; 10YR 6/2 dry) gravelly clay loam; weak fine and medium granular structure; slightly sticky, slightly plastic; few patchy faint brown (10 YR 4/3) clay films on vertical ped faces; common fine to coarse roots throughout horizon; common tubular discontinuous fine and medium and common fine tubular pores; 25% subangular blocky mixed shale and sandstone gravels; neutral (pH 7.0); abrupt smooth boundary.</p> <p><b>Bt1</b>—38 to 76 cm; brown (7.5 YR 5/4) very gravelly coarse sandy clay loam; weak fine and medium subangular blocky structure; sticky, plastic; common discontinuous distinct dark brown (7.5 YR 5/4) clay films on ped faces; few fine and medium roots in cracks; common irregular medium pores; 40% subangular blocky mixed shale and sandstone gravels and channers; neutral (pH 7.0); clear wavy boundary.</p> <p><b>2Bt3</b>—107 to 147 cm; brown (7.5 YR 5/3) extremely channery sandy clay loam; weak moderate and coarse subangular blocky structure; nonsticky, nonplastic; few fine prominent pinkish gray (7.5 YR 6/2) Fe depletions and few medium prominent strong brown (7.5 YR 5/6) masses of Fe accumulation in the matrix; common distinct discontinuous brown (7.5 YR 5/4) clay films on ped faces; many coarse irregular pores; 85% subangular blocky mixed shale and sandstone channers; strongly acid (pH 5.5); clear smooth boundary.</p>	<p><b>Ap2</b>—20 to 38 cm; brown (10 YR 4/3) channery clay loam; weak medium subangular blocky parting to weak fine and medium granular structure; slightly sticky, slightly plastic; few patchy faint brown (10 YR 5/3) clay films on vertical ped faces; many moderate and coarse roots throughout horizon; common tubular discontinuous fine and medium and common coarse tubular pores; 25% subangular blocky mixed shale and sandstone channers; moderately alkaline (pH 8.0); abrupt smooth boundary.</p> <p><b>Bt2</b>—76 to 107 cm; strong brown (7.5 YR 4/6) channery sandy clay loam; moderate moderate and coarse subangular blocky structure; sticky, plastic; few fine distinct strong brown (7.5 YR 5/6) masses of Fe accumulation in the matrix; common discontinuous distinct brown (7.5 YR 5/4) clay films on ped faces; few fine roots between peds; common medium irregular pores; 30% subangular blocky mixed shale and sandstone channers; strongly acid (pH 5.5); clear wavy boundary.</p> <p><b>2Bt4</b>—147 to 172+ cm; strong brown (7.5YR 5/6) extremely channery sandy clay loam; weak extremely coarse prismatic structure parting to moderate coarse subangular blocky structure; slightly sticky, slightly plastic; common moderate prominent light brown (10 YR 6/2) Fe depletions and common coarse prominent strong brown (7.5 YR 5/8) masses of Fe accumulation in the matrix; common distinct discontinuous brown (7.5 YR 5/4) clay films on ped and rock fragment faces; few fine irregular pores; 75% subangular blocky mixed shale and sandstone channers; moderately acid (pH 6.0).</p>

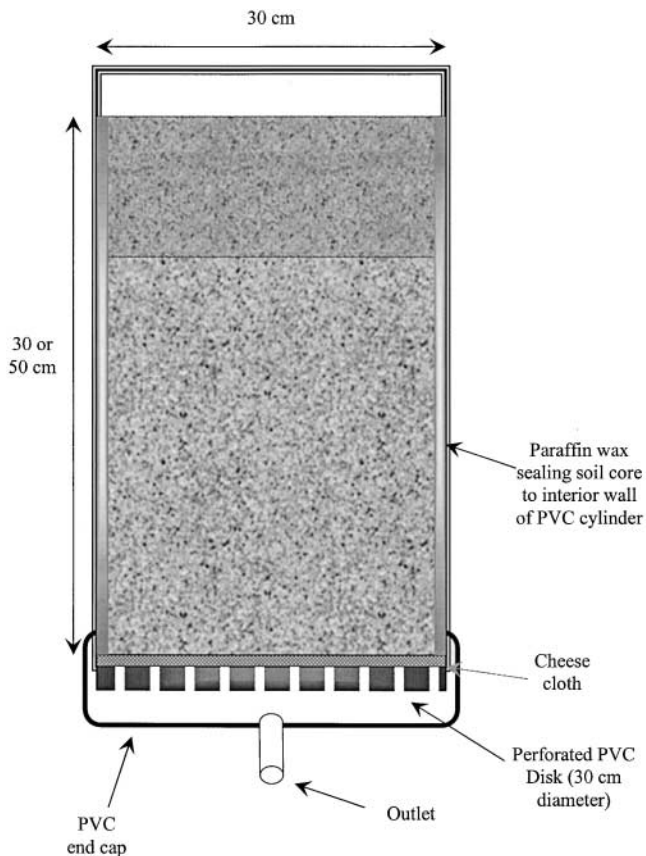


Fig. 3. Soil core leaching setup employed in the study (adapted from McDowell and Sharpley, 2001b).

tation event with a 1-yr return period. Leachate was collected daily and stored at 4°C until analyzed.

### Laboratory Analysis

Tile drainage and leachate from the soil columns were analyzed for dissolved reactive P (DRP) by filtering water samples (0.45 µm) and analyzing the filtrate colorimetrically by the method of Murphy and Riley (1962). Total P was measured on unfiltered leachate by modified semimicro-Kjeldahl procedure following Bremner (1996).

Soil samples were subjected to extraction with distilled water (Kuo, 1996), Mehlich-3 solution (Mehlich, 1984) and acid ammonium oxalate (Ross and Wang, 1993). Distilled water extraction was conducted by shaking 0.5 g of soil in 5-mL of distilled water for 1 h. Mehlich-3 and water soluble P concentrations were determined colorimetrically (Murphy and Riley, 1962). Acid ammonium oxalate P, Fe, and Al concentrations were determined by inductively coupled plasma-atomic emission spectroscopy. For each soil extraction, four bulk horizon samples were analyzed to estimate variance within the horizons. Because of limited sample size, clay films, Fe concentrations, and Fe depletions were only analyzed in duplicate.

Soil P sorption saturation was determined from the acid ammonium oxalate data, as detailed in Kleinman and Sharpley (2002):

Table 2. Properties of poultry manure used in leaching experiment.

Dry matter, %	53
pH	8.9
Total P, mg kg <sup>-1</sup>	13 725
Total N, g kg <sup>-1</sup>	20.9
Organic C, g kg <sup>-1</sup>	127
C/N Ratio	6.1

$$P_{\text{sat}} = \frac{P_{\text{ox}}}{(\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})} \times 100$$

where  $P_{\text{ox}}$ ,  $\text{Fe}_{\text{ox}}$ , and  $\text{Al}_{\text{ox}}$  denote acid ammonium oxalate extractable P, Fe, and Al, respectively, represented as millimoles per kilogram (mmol kg<sup>-1</sup>).

Particle-size analysis was conducted on bulk samples by the hydrometer method (Gee and Bauder, 1986).

### Data Analysis

Only bulk samples laboratory analysis was replicated to allow for statistical analysis. To statistically evaluate profile trends in soil P (i.e., P concentrations related to bulk and clay film samples), differences in bulk sample concentrations between individual horizons were assessed by ANOVA (Neter et al., 1996). Because clay film samples were collected in very small quantities, only single replicates were obtained. Therefore, to quantify trends we observed in clay film data, we made the assumption that the variance within the clay film data was equal to the variance observed with the bulk samples. Pair-wise comparisons were conducted by Student's *t* test (Snedecor and Cochran, 1991).

## RESULTS AND DISCUSSION

### Soil Morphology

Morphological descriptions are given in Table 1. The clay films of the argillic horizons in these soils are thick and distinctly colored. Clay films are clearly visible on open root channels and along faces of peds, and likely coat surfaces of both active macropores and interiors of pores that are now plugged with illuvial material (i.e., inactive macropores). Given the difficulty in differentiating between active and inactive macropores, the clay film scrapings collected in this study could not be restricted solely to macropores contributing to P transport.

In the county-level soil survey, the permeability of Buchanan soils is listed as 1.5 to 5.1 cm h<sup>-1</sup> in the Ap and Bt horizons and 0.2 to 0.5 cm h<sup>-1</sup> in the fragipan (Eckenrode, 1985). The permeability of Hartleton soils is listed as 1.5 to 15 cm h<sup>-1</sup> throughout the solum. Despite the contrasting permeabilities of Buchanan and Hartleton soils, macropore distribution in these soils is likely more important to P transport, given the processes described above. Macropores were abundant within the subsurface horizons of all three soils, as reflected by visually observable pores in the argillic horizons (quantified as "common" in all three soils), well-expressed structural properties (subangular blocky to prismatic), clay films, and root distributions (Table 1).

The Lower and Upper Buchanan soils have well-developed fragipans. Fragic properties are well expressed

**Table 3. Phosphorus and textural properties of three soils included in study.**

Horizon	Depth cm	Fraction	P <sub>ox</sub> <sup>†</sup>		Al <sub>ox</sub> + Fe <sub>ox</sub>		P <sub>sat</sub>		H <sub>2</sub> O soluble P		Mehlich-3 P		Particle-size distribution		
			mean	st. dev.	mean	st. dev.	mean	st. dev.	mean	st. dev.	mean	st. dev.	Sand	Silt	Clay
cm			— mg kg <sup>−1</sup> —		— mmol kg <sup>−1</sup> —		— % —		mg kg <sup>−1</sup>						
Lower Buchanan															
Ap1	0–12	Bulk	284	35	92	1	10.0	0.02	2.3	0.55	45.0	3.4	220	515	265
Ap2	12–25	Bulk	168	15	90	3	6.0	0.20	1.3	0.29	11.0	0.4	201	534	265
Bt1	25–45	Bulk	10	3	35	3	0.9	0.08	0.4	0.11	1.7	0.2	217	506	277
Bt2	45–62	Clay film	20		23		2.7		0.8		2.5				
		Bulk	7	2	45	9	0.5	0.10	0.2	0.05	0.9	0.1	207	523	270
2Btx1	62–105	Clay film	8		26		1.0		0.2		1.1				
		Bulk	19	4	40	2	1.5	0.08	0.2	0.02	1.3	0.2	281	464	255
2Btx2	105–130+	Clay film	9		24		1.3		0.1		1.0				
		Bulk	44	6	55	1	2.6	0.04	0.1	0.06	4.9	0.6	408	331	261
		Clay film	39		41		3.0		0.1		3.2				
Upper Buchanan															
Ap1	0–15	Bulk	279	34	83	1	10.8	0.02	4.4	1.26	65.8	7.2	160	538	302
Ap2	15–27	Bulk	143	16	92	1	5.0	0.07	1.3	0.33	9.8	0.5	133	565	302
Bt1	27–55	Bulk	12	5	64	5	0.6	0.05	0.5	0.18	1.5	0.3	195	389	415
Bt2	55–95	Clay film	10		23		1.3		0.2		1.3				
		Bulk	5	2	46	13	0.3	0.10	0.2	0.11	1.3	0.2	80	534	386
2Btx1	95–120	Clay film	7		31		0.8		0.2		1.7				
		Bulk	7	1	40	1	0.6	0.01	0.5	0.12	0.7	0.1	123	549	327
2Btx2	120–160+	Clay film	6		30		0.7		0.2		1.1				
		Bulk	24	4	42	1	1.8	0.04	0.1	0.03	0.7	0.1	349	328	323
		Clay film	13		25		1.6		0.1		1.4				
Hartleton															
Ap1	0–20	Bulk	417	32	61	3	22.0	1.00	13.5	2.48	176.8	12.7	405	285	310
Ap2	20–37.5	Bulk	251	25	57	1	14.2	0.20	4.2	0.33	59.5	6.7	404	293	303
Bt1	38–76	Bulk	11	2	22	4	1.6	0.30	1.9	0.28	2.9	0.4	482	223	296
Bt2	38–76	Clay film	16		24		2.1		0.3		3.0				
		Bulk	23	2	50	14	1.5	0.40	0.5	0.19	3.0	0.5	533	191	276
2Bt3	76–107	Clay film	13		20		2.0		0.4		2.7				
		Bulk	19	5	17	2	3.7	0.40	0.7	0.12	6.6	0.3	552	151	298
2Bt4	107–147	Clay film	37		24		4.9		0.5		8.0				
		Bulk	24	3	21	3	3.7	0.60	1.3	0.14	8.6	0.8	Ins. S.‡	Ins. S.‡	Ins. S.‡
	147–172+														

†  $P_{ox}$ , oxalate-extractable P;  $Al_{ox}$ , oxalate-extractable Al;  $Fe_{ox}$ , oxalate-extractable Fe;  $P_{sat}$ , P sorption saturation.

‡ Ins. S., Insufficient sample to conduct analysis.

including brittleness, excavation difficulty, and lack of roots in the matrix. The absence of a fragipan in the Hartleton soil is most likely because of the high rock fragment content (extremely channery). The fragipans cause seasonally perched water tables, as reflected by the somewhat poorly drained classification, and are key to the variable source area hydrology of this location (Gburek and Sharpley, 1998). In addition to serving as a cause of saturation-related overland flow, fragipan-perched water tables can possess substantial lateral flow that may be an important P transport mechanism (Reuter et al., 1998). Therefore, in these soils, tile drains enhance the transport of P to the stream channel.

Finally, the lithologic discontinuity within the solum of all three soils is of particular note to this investigation (Table 1). The discontinuity is demarcated by a rapid change in rock fragment content, and rock fragment characteristics (e.g., type, color, and grain size). In the Lower Buchanan, horizons beneath the discontinuity exhibit a redder hue. This layering of materials within the solum is likely a result of spatially variable processes operating during colluviation. Trends in P distribution related to the lithologic discontinuity are discussed in the following section.

### Interpreting Phosphorus Distribution with Depth

Chemical analyses of samples taken from individual horizons reveal similar gross trends in P distribution within the three soil profiles. Table 3 presents chemical

and physical properties for each profile, differentiating bulk samples from clay-film samples.

### Oxalate-Extractable Elements

Acid ammonium oxalate extracts amorphous sesquioxides that account for the bulk of P sorption capacity in acidic soils (Jackson et al., 1986; Freese et al., 1992). In general,  $P_{ox}$  declines sharply from its maximum concentrations in the Ap1 horizons (279–417  $mg\ kg^{-1}$ ) that are enriched annually with manure P. Oxalate P reaches its lowest concentrations in the upper argillic (Bt1 and Bt2) horizons (2–23  $mg\ kg^{-1}$ ), and increases slightly below the lithologic discontinuity (13–44  $mg\ kg^{-1}$ ).

Soil  $P_{ox}$  data do provide some evidence of P leaching via soil macropores. Specifically,  $P_{ox}$  concentrations in the clay films of four of the subsoil horizons (Bt1 of Lower Buchanan, Bt2 of Upper Buchanan, Bt1 and 2Bt3 of Hartleton) are significantly higher than  $P_{ox}$  concentrations in corresponding bulk samples ( $P < 0.05$ ) (Table 3). This suggests that P has been translocated along soil macropores, possibly as colloidal P during leaching or as dissolved P that is now sorbed to macropore walls. The elevated  $P_{ox}$  concentrations (37  $mg\ kg^{-1}$ ) in the clay films of the 2Bt3 horizon of the Hartleton soils occur at the approximate depth of artificial drainage, indicating the potential for environmental losses of leached P. However, such observations and interpretations must be tempered with the fact that an

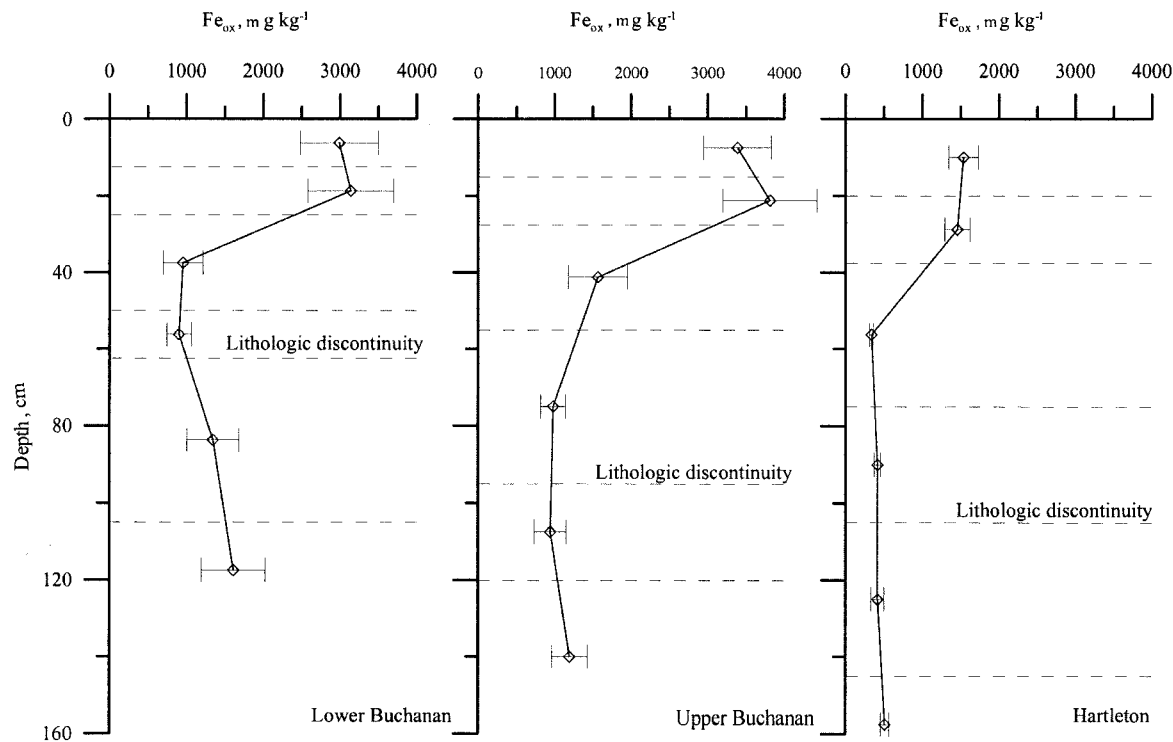


Fig. 4. Distribution of oxalate-extractable Fe in soil profiles. Error bars represent one standard deviation around the mean of the bulk observation.

equal number of horizons exhibited the opposite trend, with  $P_{ox}$  significantly lower in the clay films than in the bulk samples. Here it is important to reiterate that not all clay films are necessarily associated with active macropores. Rather, some clay films may belong to macropores that are now discontinuous with surface horizons, while others may represent plugged macropores that are no longer functional as conduits for bypass flow.

The enhanced mobilization of P under reducing conditions because of saturation has been well documented (e.g., Jensen et al., 1998). Reduction of Fe from the ferric ( $Fe^{3+}$ ) to ferrous ( $Fe^{2+}$ ) state results in the dissolution of Fe phosphates. Following dissolution, P may leach lower within the soil profile where it is resorbed following oxidation. One striking trend observed in all three soils is that  $P_{ox}$  concentrations in the lower solum are significantly higher than in the upper argillic horizons ( $P < 0.001$ ). Such a disparity in  $P_{ox}$  concentrations could result from the dissolution and mobilization of P from saturated and reduced overlying argillic horizons (Table 3). Trends in bulk sample  $Fe_{ox}$  with depth reveal significantly greater  $Fe_{ox}$  concentrations ( $P < 0.05$ ), and hence greater P sorption capacity, below the lithologic discontinuity where  $P_{ox}$  concentrations are greater than in the overlying argillic horizons (Fig. 4).

### Soil Phosphorus Sorption Saturation

Soil P sorption saturation has been linked to P leaching potential in a variety of studies (Breeuwsma and Silva, 1992; McDowell and Sharpley, 2001b). As  $P_{sat}$  incorporates both sorbed P ( $P_{ox}$ ) and P sorption capacity ( $Fe_{ox} + Al_{ox}$ ) in its calculation, differences in  $P_{sat}$  distribution by horizon as well as by morphological fraction

(bulk and clay film) offer valuable insight into trends affecting the potential for P movement. Near the surface,  $P_{sat}$  in bulk soil samples range from 11 to 22%, whereas subsoil  $P_{sat}$  ranges from 0.2 to 3.7%. Annual fertilization through manure additions and subsequent sorption of added P clearly explain the high  $P_{sat}$  of the Ap horizons. Most trends observed in  $P_{sat}$  appear to follow those of  $P_{ox}$  described above. In all three soils,  $P_{sat}$  increases significantly ( $P < 0.05$ ) below the lithologic discontinuity. Phosphorus sorption saturation is elevated in most clay films (0.7–5%) relative to corresponding bulk samples, offering further evidence of P transport via preferential flow pathways (Table 3).

### Water-Soluble Phosphorus

Water-soluble P is an indicator of P readily available to the soil solution, and is strongly correlated with DRP losses in runoff (Pote et al., 1999). Elevated water soluble P at depth would suggest that these soils have a potential to desorb P to drain water. Water-soluble P declines from the surface (1.3–13.5  $mg\ kg^{-1}$ ) to the subsoil (0.1–1.9  $mg\ kg^{-1}$ ), with the highest concentrations occurring in the surface and subsurface horizons of the Hartleton soil (Table 3). In the subsoil, water-soluble P is significantly higher in the Bt1 horizons of all soils than in lower horizons ( $P < 0.05$ ). The changes in water-soluble P with depth highlight the role of manure additions as a source of this highly labile fraction, as well as the high P buffering capacities of the subsoil, which result in low absolute concentrations. The high water-soluble P concentrations in the bulk samples of the Bt1 horizons, relative to the lower argillic horizons, indicate limited translocation of soluble P from the soil surface

horizons, possibly by matrix flow. However, the absence of elevated concentrations of water-soluble P lower in the profile, where artificial drainage is installed, indicates that leaching of water-soluble P through the soil matrix may not be important to subsurface P transport in these soils.

Unlike  $P_{ox}$  and  $P_{sat}$ , we anticipated significantly lower water-soluble P in the clay films than in the bulk samples because of increased sorption of solution P in the clay films related to their greater reactive surface area and elevated sorption capacities ( $Al_{ox} + Fe_{ox}$ ). In five of the eleven clay film samples (Lower Buchanan 2Btx1, Upper Buchanan Bt1 and Bt3 and Hartleton Bt1 and 2Bt3) water-extractable P is significantly lower than in the corresponding bulk samples (Table 3). Notably, in one horizon (the Lower Buchanan Bt1 horizon), water-extractable P was significantly higher in the clay film than in the bulk sample. In this case, the clay film sample had a considerably high  $P_{sat}$  (3%) relative to the bulk sample (1%), which may explain the elevated water-extractable P concentration, as P desorption to water is strongly correlated with  $P_{sat}$  (Sharpley and Rekolainen, 1997).

### Mehlich-3 Phosphorus

Mehlich-3 P, an indicator of plant available P, ranges from 9 to 177 mg kg<sup>-1</sup> at the soil surface to 0.3 to 3.0 mg kg<sup>-1</sup> in the argillic horizons and 1.4 to 8.6 mg kg<sup>-1</sup> below the lithologic discontinuity (Table 3). As a point of reference, in Pennsylvania, a crop response threshold has been estimated at a Mehlich-3 P concentration of 65 mg kg<sup>-1</sup>, above which the addition of fertilizer P is not expected to increase crop yield (Beegle, 1999). As such, Mehlich-3 P concentrations in the surface horizons of the Upper Buchanan and Hartleton soils are well in excess of crop requirements. Mehlich-3 P concentrations in the surface horizon of the Lower Buchanan soil are below crop requirements. Trends with Mehlich-3 P are similar to those with  $P_{ox}$ , and both are highly correlated ( $r = 0.90$ , Mehlich-3 P =  $0.3 P_{ox} - 4.8$ ). As with  $P_{ox}$ , Mehlich-3 P concentrations were significantly greater in six of the eleven clay-film samples relative to corresponding bulk samples. Similarly, the Mehlich-3 P concentration of the C horizons (1.4–7.5 mg kg<sup>-1</sup>) was not significantly different from those below the lithologic discontinuity, again indicating an authigenic cause of elevated P below the lithologic discontinuity.

### Origin of Phosphorus in the Lower Solum

To further deduce whether elevated P in the lower solum resulted from long-term leaching or from varied parent materials within the regolith, we collected samples beneath the solum of each of the three soils (approximately 2-m depth). Concentrations of  $P_{ox}$  (12–20 mg kg<sup>-1</sup>) in the C horizon cores are not significantly different from the lower solum concentrations ( $P > 0.1$ ). Similarly,  $P_{sat}$  in the C horizons (2–3%) is not significantly different from  $P_{sat}$  in the lower solum ( $P > 0.1$ ). Thus, the elevated P concentrations in the lower solum appear to be authigenic (i.e., because of a discontinuity in soil parent materials). It is unlikely that leaching of surface-applied manure P would uniformly enrich the matrices of the lower solum and C horizons and that sufficient manure P has been translocated to account for the mass of  $P_{ox}$  found in the regolith.

### Leaching Observations

Table 4 presents leachate DRP, TP, and volume data from the soil columns. Prior to manure addition, leachate DRP concentrations ranged from 0.004 to 0.011 mg L<sup>-1</sup> and TP ranged from 0.047 to 0.308 mg L<sup>-1</sup>, while leachate DRP loads ranged from 0.009 to 0.042 mg and leachate TP loads ranged from 0.107 to 1.026 mg. On average, DRP accounted for only 5% of TP concentration. No statistically significant ( $P > 0.05$ ) differences in leachate P concentrations and loads were observed between the 30-cm deep cores, representing leaching potential to the argillic horizon, and the 50-cm deep cores, representing leaching potential to the lower solum and tile drainage (Table 4).

Following poultry-manure application, mean concentrations of leachate DRP and TP were significantly higher than before manure application ( $P < 0.05$ ), as were mean loads ( $P < 0.03$ ) (Table 4). On average, DRP accounted for 73% of TP concentration after manure application, as opposed to 5% of TP before manure application. Total P loads (mg) in leachate represented 0.03 to 1.11% of TP applied to the columns in manure. As before manure addition, leachate P concentrations did not differ significantly ( $P > 0.05$ ) between 30-cm and 50-cm deep cores.

Results from the leaching experiment indicate the importance of manure addition to P leaching, and confirm the potential to leach P to the lower solum, approximately the depth of the tile drain, in all three soils. As

**Table 4.** Leachate P concentrations from soil cores before and after manure addition.

Soil	Before manure application						After broadcasting 85 kg ha <sup>-1</sup> Total P in poultry manure							
	Core depth	Leachate volume	DRP†	TP	DRP	TP	Leachate volume	DRP	TP	DRP	TP	Manure P leached		
												DRP	TP	
	cm	mL	— mg L <sup>-1</sup> —		— mg —		mL	— mg L <sup>-1</sup> —		— mg —			%	
Lower Buchanan	30	2261	0.005	0.047	0.011	0.107	1000	0.034	0.181	0.034	0.181	0.01	0.03	
Lower Buchanan	50	3329	0.013	0.308	0.042	1.026	1776	2.833	3.735	5.031	6.633	0.84	1.11	
Upper Buchanan	30	2733	0.004	0.127	0.011	0.346	2087	1.938	2.408	4.044	5.024	0.67	0.84	
Upper Buchanan	50	2529	0.005	0.101	0.012	0.255	3640	1.031	1.402	3.753	5.102	0.63	0.85	
Hartleton	30	1889	0.005	0.125	0.009	0.236	3954	0.609	1.015	2.408	4.014	0.40	0.67	
Hartleton	50	2282	0.006	0.087	0.014	0.198	3360	0.079	0.205	0.267	0.689	0.04	0.11	

† DRP, dissolved reactive P; TP, total P.

manure was added at a rate corresponding with the annual average, and manure is typically applied to these soils in the spring, when soils are wet, it is likely that this experiment accurately simulates field conditions.

Because there was no systematic difference in leachate P losses between the 30- and 50-cm deep cores, results suggest that P is transported via preferential flow pathways. If matrix flow was the dominant mechanism of subsurface P transport, then one would expect P concentrations in leachate to be greater from the 30-cm cores than from the 50-cm cores. In fact, the greatest leaching losses (concentrations and loads) among all replicates were consistently observed from a 50-cm core (Lower Buchanan). Furthermore, the ranking of TP losses from individual cores after manure application was identical to the ranking of TP losses prior to manure application, such that the Lower Buchanan 50-cm core consistently had the highest losses while the Lower Buchanan 30-cm core had lowest losses. Such a consistent response illustrates that P transport from the soil surface, particularly from manure P, is responsible for subsurface P concentrations and that an active macropore flow pathway is necessary for P transport.

Monitoring of tile drainage from May to October 2000 further supports the importance of subsurface flow as a pathway for P loss from these soils (Table 5). Mean (flow weighted) drainage DRP concentrations ranged from 0.010 mg L<sup>-1</sup> during base flow to 0.102 mg L<sup>-1</sup> during storm event flow. Mean TP concentrations ranged from 0.019 mg L<sup>-1</sup> during base flow to 0.283 mg L<sup>-1</sup> during storm event flow. Although base flow volume (458 895 L) was greater than storm flow volume (58 935 L), loads of DRP and TP were substantially higher during storm flow than during base flow. Increases in drainage P concentrations during storm flow more than offset the greater flow volumes observed during base flow. The elevated losses of P in tile drainage during storm events support the conclusion that rapid, subsurface P transport can be significant within this system. In fact, storm flow concentrations are frequently above eutrophic criteria (0.1 mg L<sup>-1</sup> as TP) established for streams or other flowing waters not discharging directly into lakes or impoundments (Dodds et al., 1998; U.S. Environmental Protection Agency, 1994).

Concentrations of DRP and TP in leachate from the 30- and 50-cm lysimeters before manure addition were

not correlated to any of the soil P fractions (P<sub>ox</sub>, P<sub>sat</sub>, water soluble P, Mehlich-3 P), nor to Fe<sub>ox</sub>, measured in bulk and clay-film samples taken from corresponding depths ( $P > 0.1$ ). Nor were concentrations of soil P fractions from surface (Ap1) horizons correlated with leachate P concentrations ( $P > 0.3$ ). These poor correlations indicate that profile P data provide poor quantitative prediction of P leaching potential.

## CONCLUSIONS

Despite strong evidence of water-soluble P translocation in bulk samples of shallow subsoil horizons, samples collected deeper in the profile exhibited no evidence of such translocation. As such, leaching of dissolved P from the matrix of these soils is likely not of environmental importance. However, the most compelling evidence that P leaching had occurred in these soils was provided by clay-film samples, some of which exhibited significantly elevated P<sub>ox</sub>, P<sub>sat</sub>, and Mehlich-3 P concentration relative to bulk samples. This indicates that subsurface P transport via macropores may occur to tile-drain depths. Not all clay films, however, possessed P concentrations greater than the bulk samples. Nor were all clay films necessarily associated with active macropores.

Increases in P<sub>ox</sub>, P<sub>sat</sub>, and Mehlich-3 P concentrations in bulk samples of the lower solum may be explained by two competing theories: (i) discontinuity in parent material (at the fragipan boundary in Buchanan soils); and, (ii) preferential flow of P from the soil surface to the lower horizons (i.e., bypass leaching). Based upon P profile data alone, we cannot discount the first theory, as rock fragment quantity and type differences within the subsoil indicate that two stratified parent materials are present in all three soils.

This study shows that soil P profile data must be carefully interpreted to properly assess P leaching potential. Bulk horizon samples appeared to provide evidence of P translocation, but the elevated P in the subsoil was ultimately attributed to lithological differences. The need for scrutiny of P profile data is because of the dominant mechanism of subsurface P transport: preferential flow. Leachate P bypasses the matrix of subsoil horizons via select macropores that are not taken into account by bulk sampling of horizons. Indeed, leaching experiments confirmed that the potential to leach P to the depth of artificial drainage was equivalent to the potential to leach P to shallow depths. Monitoring data revealed an increase in drainage P concentrations with flow, providing clear indication of the importance of bypass flow via soil macropores.

The transport of P by subsurface pathways can be an important mechanism of P transfer from land to water in heavily manured soils, especially those that are artificially drained or have preferential flow pathways connected to stream channel discharge. This study reveals that detailed description and interpretation of soil P profile data provides limited insight into P leaching potential: correlation of soil P fractions with leachate P from lysimeters was poor.

**Table 5. P losses in tile drainage from May to October, 2000.**

Flow regime	Concentration†		Drainage volume	Load‡	
	DRP	TP		DRP	TP
	— mg L <sup>-1</sup> —			— g —	
Base flow					
Mean	0.010	0.019	458 895	4.6	8.7
Maximum	0.012	0.023			
Minimum	0.009	0.014			
Storm Flow					
Mean	0.102	0.283	58 935	6.0	16.7
Maximum	0.146	0.498			
Minimum	0.056	0.099			
Total Flow	0.020	0.049	517 830	10.6	25.4

<sup>†</sup> DRP, dissolved reactive P; TP, total P.

<sup>‡</sup> Load = mean concentration × total drainage volume.

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